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DRAWINGS ATTACHED

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(54) GALVANIC STORAGE UNITS

(71) We, DEUTSCHE AUTOMOBILGESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, of 136, Mercedesstrasse, Stuttgart 60 (Unterturkheim), Germany, a Company organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a galvanic storage unit, more particularly, but not exclusively, for traction purposes and having in a common housing an accumulator device which is capable of providing relatively high currents for short periods, and a fuel cell device connected in parallel therewith. Galvanic systems have become known—e.g. the lead accumulator—which are capable of reversibly delivering electrical energy and storing it again in the form of chemical energy. Energy values referred to mass or to volume of 40 Wh/kg or 90 Wh/dm³ can be obtained with such systems if it is not desired to adopt systems involving very expensive materials such as for example are used in the Ag/Zn accumulator. However, accumulators of this type are not suitable for industrial application in the traction field.

It has been proposed to replace the negative electrode in a conventional accumulator —e.g. by a Raney nickel electrode (German Patent Specification No. 1,118,843) or a titanium hydride electrode. These electrodes are suitable for storing the active material (in this case hydrogen) with a higher charge density than is customarily the case with negative electrodes. Moreover, further electrochemical advantages result from this due to the fact that the electrochemically active material does not have to be built up in the form of a crystallographic lattice during deposition (i.e. during the charging process). When such a negative electrode is used, an accumulator having substantially more favourable energy values for traction is obtained, e.g.:—

Lead accumulator	=35 Wh/kg
Ni/Cd accumulator	=40 Wh/kg
$TiH_x/NiO(OH)_2$ accumulator	=70 Wh/kg

The fact that only a value of 70 Wh/kg can be realised for this accumulator, despite the high energy to mass ratio of the negative electrode which is 400 Wh/kg, is due to the fact that the positive electrode exhibits values of only approximately 100 Wh/kg.

One might possibly consider using the air electrode known from fuel cell technique instead of the positive electrode here. Since it does not work as a storage electrode, but utilises the surrounding atmosphere as an oxygen storage unit, it naturally exhibits a high charge to mass ratio.

It would therefore be possible to achieve values of 140 Wh/kg for a cell or battery. The disadvantage of such an arrangement is that due to the limited load capacity of the air electrode—particularly if the noble metals are not used as catalysts for reasons of economy —the power density (W/cm²) of the electrodes is small. Thus the following comparative values are obtained:—

Lead accumulator	0.03 . . 0.1 W/cm²
$TiH_x/NiO(OH)_2$ accumulator	0.05 . . 0.14 W/cm²
TiH_x/air cell	0.04 . . 0.06 W/cm²

Considering now the application to traction, where high power outputs are required for peak loads such as at starting, it becomes necessary for a TiH_x/air battery—also described hereinafter as an example of a fuel cell device—to be combined with an accumulator which is charged continuously by the battery and which supplements the battery to provide the high power outputs. This causes the initially advantageous energy to weight ratio to be seriously impaired.

It is the aim of the invention to provide a galvanic storage unit which is capable of delivering the currents required for the permanent load and also for the peak loads, and which at the same time permits surprisingly

high energy to mass and to volume ratios to be obtained.

This aim is achieved according to the invention in that the accumulator device and the fuel cell device have a common reversible negative electrode. This eliminates an O_2-deposition electrode as charging electrode for charging the accumulator.

It is advantageous if a porous separator is provided between the common electrode and the positive electrode of the fuel cell so as to separate the two electrodes electrically whilst connecting them mechanically. In this way all the electrodes can remain in a common electrolyte and the positive electrode of the fuel cell can be nevertheless supported mechanically by the separator by being connected mechanically to the common negative electrode by the separator. Such a separator may be made of asbestos.

It is advantageous in the case of a storage unit forming a double fuel cell and accumulator system if the two fuel cell devices are arranged in mirror image symmetry on either side of a positive electrode. By this means again the energy to mass and volume ratios are increased, because a common positive electrode is used for the two accumulator devices.

It is helpful if the common negative electrode is a hydrogen storage electrode. This measure procures a high Wh/kg value.

Further advantages and features of the invention will be clear from the description hereinbelow of two exemplary embodiments. In the accompanying drawing:

Figure 1 shows a diagrammatic cross-section of the first embodiment,

Figure 2 shows a circuit for the first embodiment for a first mode of operation,

Figure 3 shows a circuit for the first embodiment for a second mode of operation, and

Figure 4 shows a diagrammatic cross-section of the second embodiment.

Referring to Figure 1, the galvanic unit has a housing 11 with two orifices 12 communicating with an electrolyte space 13. A positive electrode 14, consisting of $NiO(OH)_2$ as active material projects into the electrolyte space 13 from a position between the orifices 12. On the right hand side of the right hand orifice 12, a reversible negative electrode 16 projects into the electrolyte space 13 and may be a TiH_x electrode. The electrodes 14 and 16 together form an accumulator.

To the right of the electrode 16 a separator 17 is provided and is connected mechanically to the electrode 16 in manner not shown. The separator 17 is sufficiently porous for the electrolyte present in the electrolyte space 13 to rise in it. To the right of the separator 17 is an air electrode 18 which occupies one side of the housing 11 and is mechanically connected to the separator 17. The electrode 16 and the air electrode 18 together form a fuel cell. The latter is capable of delivering the steady currents, whilst the accumulator delivers the peak currents.

Figure 2 shows the circuit for such a base load operation. The load 19 in this case is connected in circuit with the fuel cell, because the switch S2 is closed. The accumulator is out of circuit because the switch S1 is open.

If it is desired to operate the galvanic storage unit on peak loads then as Figure 3 shows, the switch S1 is also closed, so that both the accumulator and the fuel cell are connected in parallel with each other to the load 19.

The arrangement therefore permits,

—the elimination of an additional buffer accumulator (instead of which only one additional electrode is required)

—the design of the positive Ni oxide electrode to be such that it stores only the energy for the power peaks (thus making it smaller and lighter)

—the elimination of an additional electrode in the TiH_x air cell, which would be required in order to have an O_2- deposition electrode in the system for charging the negative electrode.

As a result of the above-listed features, the arrangement according to the invention has simultaneously more favourable energy and power to mass and to volume ratios than the known systems (c.f. Table below).

Discharge time	h	5	5	5	5
Basic load	kW	28	28	28	28
Overload	h	0	0.5	1	1.5
	kW	0	84	84	84
Energy stored	kWh	140	168	196	224
Ti (H_2)/Ni accumulator	$\frac{wh}{kg}$	70	71	72	73
Ti (H_2)/air cell	$\frac{Wh}{kg}$	140	93	105	115
Cell according to the invention	$\frac{Wh}{—}$	140	125	115	110

Table: comparison of energy data referred to mass for various energy sources.

It is clear from the table that the galvanic cell according to the invention is definitely superior for the range from 0 to 20% overload which is relevant to traction purposes. Also taking into account the fact that the construction of air electrodes is technically more complicated and expensive than the manufacture of accumulators, and that the data stated is valid for a TiH_x/air cell at a temperature of 80°C, whereas the data for the cell according to the invention is also valid for 0—20°C., the technical advantage of the latter becomes obvious.

A second embodiment of the invention is illustrated schematically in Figure 4 and comprises a double fuel cell and accumulator system with the two fuel cell devices arranged in mirror image symmetry on either side of a common positive electrode for the two accumulator devices. In a polysulphone frame 21, which consists of glued layers, are two spaced sets of polysulphone bars 22, each of which supports an air electrode 18 on one side. Such an air electrode may be 1 mm thick and have an area of 300 cm^2. Against each air electrode is an asbestos layer 17 as separator with a thickness of 0.5 mm. Against the separator in each case is an electrode 16 of TiH_x which is 1.5 mm thick and which constitutes a reversible negative electrode common to the adjacent fuel cell and accumulator devices. This in turn is followed in each case by an electrolyte space 23 in the case of the left hand assembly and electrolyte space 24 in the case of the right hand assembly, the two spaces 23 and 24 being mutually separated by positive electrode 14, which consists of $NiO(OH)_2$ and is 1 mm thick and constitutes a common positive electrode for the two accumulator devices. An air inlet channel 26 with tap pipes 27, through which air can be passed to the air electrodes 18, is shown at the top of Figure 4. A corresponding air outlet, not shown, is also provided.

In corresponding manner, an electrolyte inlet channel 28 with tap pipes 29 is provided through which electrolyte can be supplied to the electrolyte spaces 23, 24. A corresponding electrolyte outlet (not shown) is also provided. A gas space 31, which is 1 mm wide is present between the polysulphone bars 22.

Air/carbon electrodes as described by R. G. Haldemann in the last paragraph at page 5 of the prospectus of the Cyanamid Corporation of June, 1967, may be used for the air electrodes 18. Asbestos may be used as separator. The bars 22 may also be made of material sold under the name Teflon (Registered Trade Mark); they are 4—5 mm wide and act as supports and also for gas distribution in the gas space 31.

The electrode 14 may be a porous sintered nickel element, having been impregnated with active $NiO(OH)_2$.

By virtue of the favourable energy and power to weight ratio, the galvanic storage unit described is particularly suitable for traction purposes.

WHAT WE CLAIM IS:—

1. A galvanic storage unit having in common housing an accumulator for delivering relatively high currents for short periods and a fuel cell connected in parallel therewith, wherein the accumulator and the fuel cell have a common reversible negative electrode.

2. A storage unit according to claim 1, wherein a porous separator is provided between said common electrode and the positive electrode of the fuel cell which separates the two electrodes electrically but connects them mechanically together.

3. A storage unit according to claim 1 or 2 and comprising a double fuel cell and accumulator system, wherein the two fuel cell devices are arranged in mirror image symmetry on either side of a common positive electrode for the two accumulator devices.

4. A storage unit according to any one of claims 1 to 3, wherein the common negative electrode is a hydrogen electrode.

5. A storage unit substantially as hereinbefore described with reference to and as shown in Figures 1 to 3 or Figure 4 of the accompanying drawings.

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1276260 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

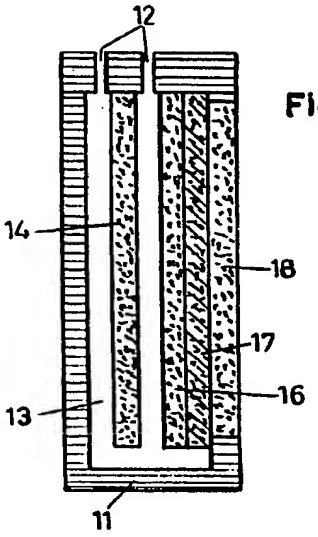
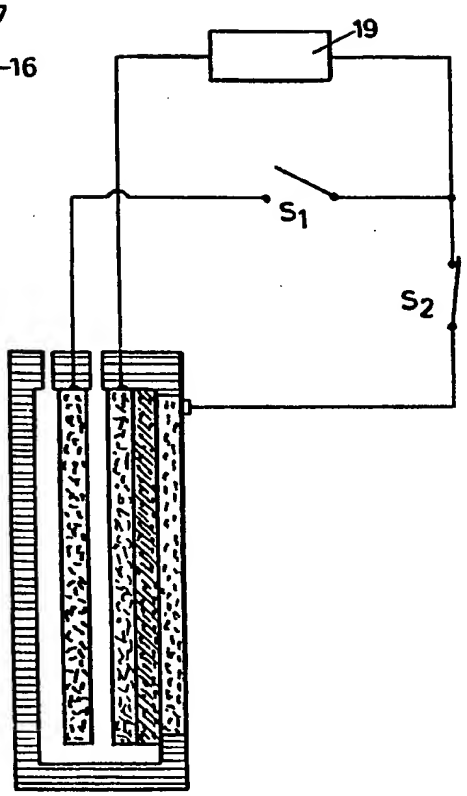


Fig.1

Fig.2



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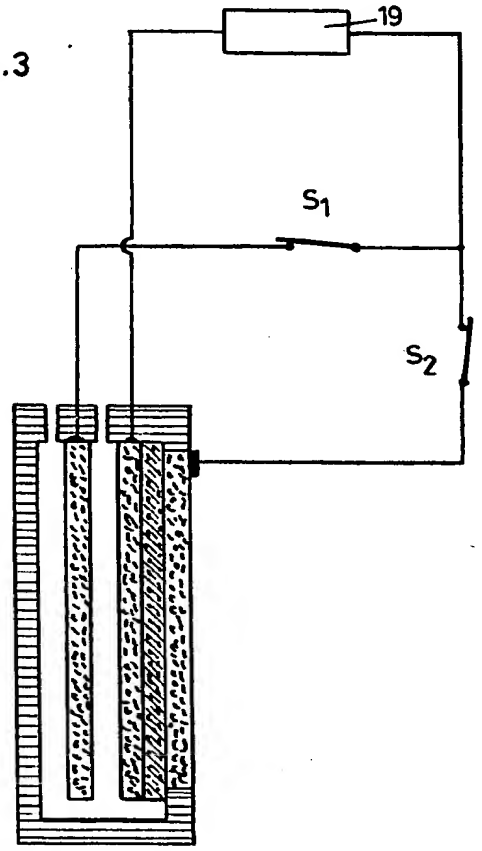
3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 2

Fig.3



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Sheet 3

Fig.4